(54) Method for selectively coating metallurgical patterns on dielectric substrates.

(57) The coating, like coating (14), is produced by selectively depositing metals, like metals (16, 17), over an existing metallurgical pattern (3) supported on or recessed in a dielectric substrate (1). The coating is formed by the following steps. Sequentially blanket coating said substrate (1) and said pattern (3) with metals, like metals (16, 17), being tuned to another in such a way that on heating a liquid metal or alloy layer, like alloy layer (18A), is formed adjacent the surface of substrate (1) and pattern (3) where said liquid layer wets said pattern (3) but not said substrate (1); heating the then present structure to a temperature where said liquid metal or said alloy layer, like layer (18A), is formed; cooling said structure; and removing said metals, like metals (16, 17), from the surface of said substrate (1) not covered by said pattern (3).

The method is applicable in selectively depositing a brazeable and solderable, protective metal coating on refractive metal conductive patterns on ceramic substrate carriers employed for mounting semiconductor devices.
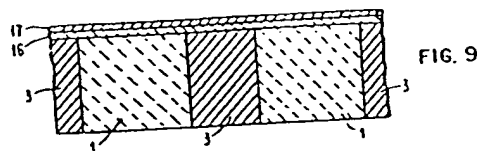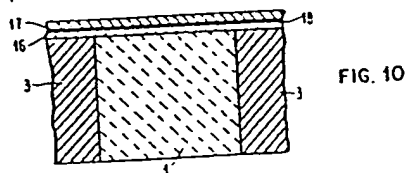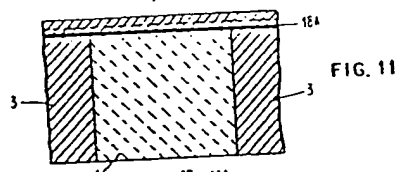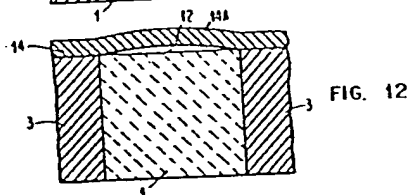
FIG. 9

FIG. 10

FIG. 11

FIG. 12

FIG. 13

0089604

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

- 1 -
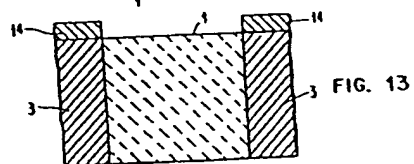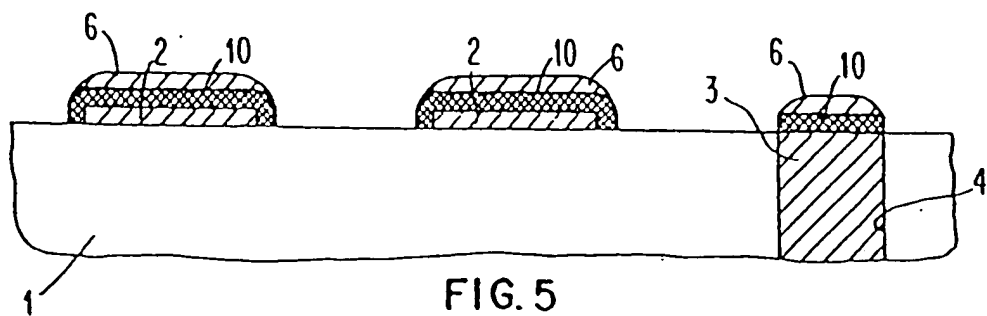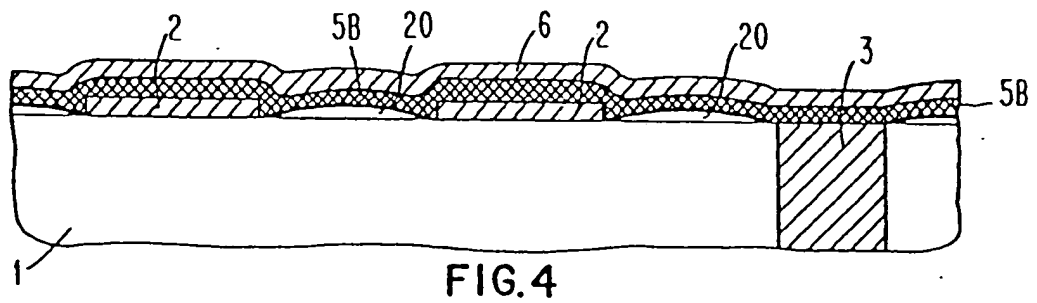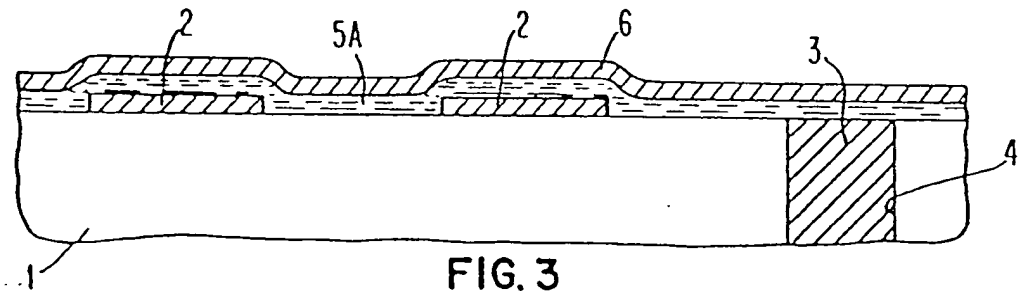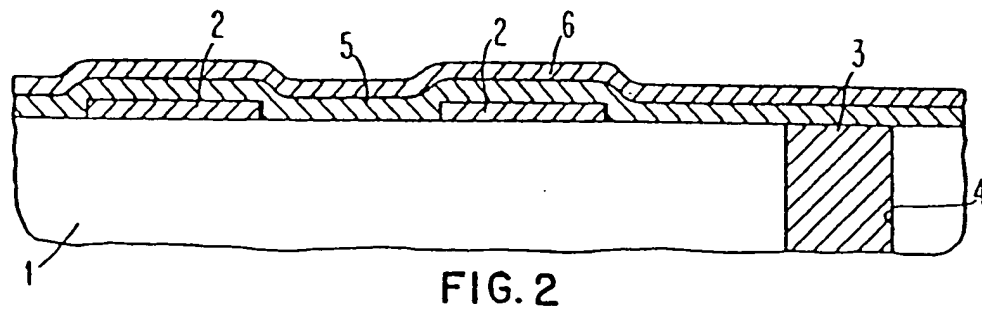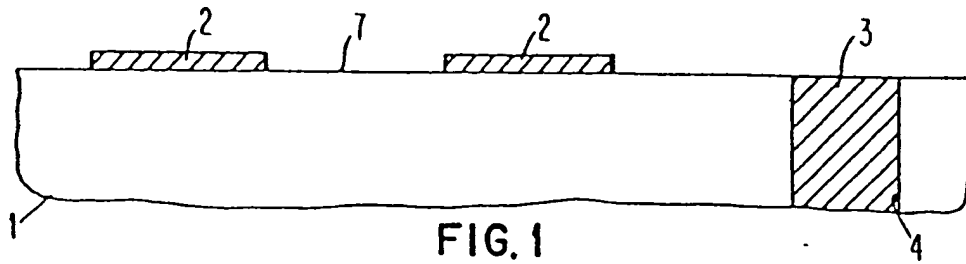
METHOD FOR SELECTIVELY COATING METALLURGICAL PATTERNS ON DIELECTRIC SUBSTRATES

The invention relates to a method for selectively depositing layers of metals over an existing metal-lurgical pattern supported on a dielectric substrate.

5   The multi-layer ceramic (MLC) technology for fabri-cating dielectric substrate carriers for integrated circuit/semiconductor package assemblies is well known. Such MLC substrates are produced by preparing a slurry of a suitable ceramic particulates (e.g. alumin), a

10   fugitive resin binder material, a solvent for the resin binder, normally with an included plasticizer; doctor blading the slurry on removable base with subsequent drying to form thin flexible sheets commonly termed ceramic green sheets. The sheets are then punched to

15   form via holes, and the via holes filled with conduc-tive metalliferous (e.g. molybdenum) paste which is also formed into a pattern of conductive lines which will ultimately form the internal circuitry of the MLC. The punched and printed green sheets are selectively

20   stacked on each other into a laminated substrate assembly, as for example, a stack of 15 to 30 green sheets, and the assembly sintered to integrate the sheets and develop the conductor pattern while removing the binder. The resultant fired MLC substrate can then

25   be employed for flip-chip mounting of semiconductor de-vices which are electrically connected to the internal circuitry of the MLC substrate.

External contact with the MLC substrate is made by a
30   plurality of I/O pins normally brazed or otherwise mounted to the opposite side of the MLC substrate to the internal circuitry thereof. It is desirable that

FI 981 031 / FI 981 032

the MLC substrate be formed with vias and lines densi-
fied in accordance with the corresponding microminia-
turization of the integrated circuit developments.
Such microminiaturization is desirable in order that
5   the package be compatible with the corresponding densi-
fied integrated circuit device chips mounted thereon.
In such application the MLC substrate must be provided
on the top surface with many small pads which are cap-
able of making registered electrical contact with cor-
10   responding closely spaced semiconductor device termi-
nals, e.g. solder mounds. In order to more efficiently
use the modern integrated circuit technology, as many
as possible integrated circuit devices are supported
on and interconnected within the MLC substrate. Such an
15   arrangement keeps the distances between interconnected
devices small and thereby minimizes the time it takes
for electrical signals to travel between the interre-
lated devices. Also this reduces the number of elec-
trical connections which must be made thereby reducing
20   the cost of the package and increases reliability. The
end result is a highly complex MLC package with a lot
of small internal printed circuitry contained in a sub-
strate carrier capable of mounting large numbers of
integrated circuit devices.

25

Further, such MLC substrates require a relatively com-
plex metallurgy on the topside to make electrical con-
nection to integrated circuit devices and to provide
engineering change pads, and on the bottom side to make
30   connection to the I/O pads, pins or other type connec-
tions. When green ceramic is sintered there is normally
a 17 to 20% shrinkage. Frequently, the shrinkage is not
uniform throughout the MLC substrate. Since the sub-
strate is relatively large, and the metallurgy geometry
35   quite small, it is difficult and frequently impossible

to produce a mask for coating protective diverse metals
on the substrate metallurgy, that is 17 to 20% smaller
than the original substrate that will have all open
areas that will coincide or register with the substrate
5 metallurgy. Such a mask is necessary for depositing
additional metallurgy metals using conventional masking
techniques. Usually the original metallurgy pattern on
the MLC substrate laminate deposited prior to sintering
and comprises a refractory (for example molybdenum)
10 metalliferous paste screened on the laminate sheets.
After sintering, the refractory metal (e.g. molybdenum,
tungsten, etc.) must not only be protectively covered
with different metals, as for example nickel, chromium,
copper, gold, etc., but also to facilitate the making
15 of connections, as by soldering, to semiconductor
devices, compression bonding to wires and/or brazing to
I/O pins. The protective coating of the refractive MLC
substrate metallurgy, where molybdenum is employed is
important, since molybdenum is susceptible to reactive
20 corrosion when exposed to humidity of any pH value at
operating potentials common in MLC module or substrate
applications. This corrosion interrupts conductors, and
leads to module failure.

25 One method of protecting the substrate metallurgy is
by covering them with diverse metals, e.g. nickel, by
electroless plating techniques which do not require
masks. However, such coatings are usually thin and may
contain impurities such as phosphorous boron, etc.,
30 which may be objectionable in subsequent joining (e.g.
soldering, brazing, compression bonding, etc.).

The protective metal layers can also be deposited by
electroplating techniques. However, such plating tech-
35 niques require electrical connection to each area to be

FI 981 031 / FI 981 032

plated, whereas in MLC substrates such connections are
not always available, since some pads or portions of
the metallurgy pattern can be "electrically floating".

5   These electroless and electroplating techniques are
expensive time consuming and difficult to control; and
thus there is a need for a maskless plating technique
which is simple with elimination of processing steps as
well as having a significant improvement in yield with-
10   out problems of phosphorous and/or boron contamination.

It is the object of the invention to provide a mask-
less, clean method for selectively metal coating an
existing metallurgical pattern on a dielectric sub-
15   strate with diverse metals or alloys.

This object is achieved by a method as defined at the
beginning of this specification having the features of
the characterizing part of claim 1.
20

The inventive method does not have the drawbacks of the
electroless selective plating methods, nor the restric-
tions of the electrochemical selective plating methods.
The inventive method is particularly useful in coating
25   a protective metal on refractive metal conductive pat-
terns on or recessed in ceramic substrate carriers em-
ployed for mounting semiconductor devices. Preferably
the invention provides a maskless method for cladding
sintered refractory metal circuit features on or re-
30   cessed in ceramic substrates with a solderable and
brazeable protective coating for connection to terminal
contacts of an integrated circuit device and to input/
output (I/O) pins.

FI 981 031 / FI 981 032

In one advantageous embodiment of the invention the
following process steps are executed

A)   sequentially blanket coating said substrate, in-
5   clusive of said pattern with discrete levels of
         diverse metals having a differential in melting
         points (a) bondable to said pattern, (b) non-wet-
         ting to the bare surface of said substrate, with
         the metal having the lowest melting point disposed
10   adjacent said substrate;

B)   heating the then present structure to a temper-
         ature above the melting point of the lower melting
         metal;
15
C)   cooling said structure to delaminate the metal
         coatings on the bare surfaces of said substrate;
         and

20 D)   removing said delaminated coatings from the bare
         surface areas of said substrate to retain a bonded
         cladding comprised of said metals on said metal-
         lurgical pattern.

25 In another advantageous embodiment of the invention the
following process steps are executed:

A)   sequentially blanket coating said substrate,
         inclusive of said pattern, with discrete levels
30   of diverse alloyable metals showing a negative
         deviation from Raoult's law in their phase dia-
         gram, with the alloy of said metals bondable to
         said pattern and non-wetting to the bare surface
         of said substrate;

B) heating the then present structure to a temper-
ature below the melting points of said metals
and above the lowest liquidus temperature in
the phase diagram of the alloy system of said
metals whereby a cladding of said metals is
bonded to said pattern and forms loosely adhered
segments on said bare surfaces of said substrate;

C) cooling said structure; and

D) removing said segments from said bare surfaces
of said substrate.

Other advantageous embodiments of the inventive method
are disclosed in the subclaims.

The invention will become more apparent from the fol-
lowing detailed description taken in conjunction with
the accompanying drawings.

Figs.	1	show schematically in cross-sectional
to	5	views, and broken sections, various
		stages of the method according to one
		advantageous embodiment of the inven-
		tion.

Figs.	6	are phase diagrams of, respectively,
to	8	palladium/nickel, gold/nickel and
		copper/gold alloy systems.

Figs.	9	are schematic cross-sectional views
to	13	showing various stages of the method
		according to another advantageous
		embodiment of the invention.

FI 981 031 / FI 981 032

Fig. 14   photographically shows the maskless
coating produced by said another ad-
vantageous embodiment to a metallur-
gical via pattern of a dielectric

5   substrate.

Fig. 15   photographically shows the maskless
coating produced by said another ad-
vantageous embodiment to engineering

10   change (EC) pads of a dielectric sub-
strate.

Fig. 16   photographically shows a cross-section
through a dielectric substrate with a

15   via metallization provided with a coat-
ing produced by said another advantage-
ous embodiment.

The liquid metallic layer required in the inventive
20   method is preferably produced in one of two ways. These
two ways are described in the following by means of two
embodiments of the inventive method. However, the inven-
tive method is not restricted to these two embodiments.
With both embodiments of the inventive method suitable
25   alloy coatings are deposited on refractory metal pat-
terns supported on or recessed in the substrate. These
alloy coatings enable further brazing and soldering to
these features.

30   First Embodiment

The method according to the first embodiment involves
depositing by such techniques as vacuum evaporation
or sputtering over the entire substrate surface dis-
35   crete layers of two metals which can form a continuous

FI 981 031 / FI 981 032

series of solid solutions whose <u>solidus</u> temperatures
lie between the melting temperatures of the pure metals,
the metal with the lower melting point being deposited
first, heating the substrate at a suitably fast heating
5   rate to slightly above the melting point of the metal
of the lower melting point to cause this layer to melt
and wet to the surfaces of the refractory metal feat-
ures and concurrently, to dewet from the ceramic sur-
face, cooling to room temperature and selectively re-
10   moving the now nonadhering metal coating on the bare
ceramic regions of the substrate surface by subjecting
the surface to the action of intense ultrasonic vibra-
tions in an inert liquid medium such as water, leaving
a strongly adherent coating of an alloy of the two me-
15   tals deposited only on the refractory metal features.
Apart from the solid solution behavior noted above, the
choice of the two metals is governed by (i) the need
for good wetting and bonding of the lower melting metal
to the refractory metal surfaces and (ii) the need to
20   ensure that the resulting alloy coating provides for
joining to these features through the use of common,
low temperature braze and solder alloys. It is to be
understood that although the ultrasonic vibration tech-
nique is the preferred method for selectively removing
25   the nonadherent metal layer from the ceramic surface
after the heat treatment step, other techniques such as
light scrubbing with a brush or vapor blasting can also
be used to accomplish this.

30   Although many binary alloy systems satisfy the cri-
terion for the solid solution behavior of the type
noted above, illustrative of two such systems are
Cu-Pd and Cu-Ni are particularly suited for this
application because (i) molten copper wets molybdenum
35   very well, forming a strong braze bond to it and (ii)

FI 981 031 / FI 981 032

the resulting alloys are easily joined to using common
brazing and soldering alloys. As a special case, we can
also obtain a single metal coating, e.g. of copper, as
opposed to an alloy coating by first depositing copper
5   on the substrate followed by depositing a thin coating
of a refractory metal such as molybdenum, which does
not form any intermetallics or solid solutions with
copper, heat treating as above to slightly above the
melting point of copper, removing the nonadhering metal
10   film on the ceramic by ultrasonic agitation, followed
by selectively etching off the molybdenun layer from
the adhering copper surface using a suitable etchant.

The principles of the method will now be illustrated
15   by taking the examples of the metals copper (melting
point 1083°C) and palladium (melting point 1575°C).
After thoroughly cleaning the substrate surface to be
rid of any oil films by standard degreasing methods,
a layer of copper (1-3 μm) is first deposited over
20   its entire surface followed by a layer of palladium
(1-3 μm) in the same pumpdown in an Ebeam evaporator.
The substrate is then heated in a nitrogen or forming
gas ambient to 1100°C at a heating rate of at least
5°C/min., held at this temperature for 5 minutes and
25   cooled at a convenient rate to room temperature. Dur-
ing the heating stage of this heat treatment, inter-
diffusion between copper and palladium layers takes
place giving rise to a series of solid solutions
ranging in composition from pure palladium at the top
30   to pure copper at the bottom closest to the substrate
surface. The heating rate used is such that, for the
thicknesses of the metal layers chosen, when the maxi-
mum heat treating temperature is reached the composi-
tion of the metal layer adjacent to the substrate sur-
35   face will be either pure copper or a dilute alloy of

FI 981 031 / FI 981 032

0089604

palladium in copper whose solidus temperature is
exceeded by the chosen peak heat treating temperature.
Under these circumstances a thin liquid metal zone is
formed next to the substrate surface during the heat
5 treatment with at least the top layers of the composite
film remaining solid. The formation of this captive
liquid zone instantaneously causes it to wet the molyb-
denum surfaces and concurrently to dewet from the bare
ceramic surface. After this is accomplished, longer
10 holding at the peak temperature would merely tend to
homogenize the composition through the composite film
without undoing the selective bonding (to the refrac-
tory metal features) and debonding (from the bare
ceramic) that had already occurred. The upper bound
15 for the peak heat treatment temperature chosen should
be such that the solidus temperature of the completely
homogenized copper-palladium alloy should be safely
above this temperature so as not to melt the entire
film. Upon cooling the substrate to room temperature
20 a continuous copper-palladium alloy film will exist on
the substrate surface, this film adhering strongly to
the refractory metal features on this surface while
staying nonadhering to the bare ceramic in the manner
of a conventional decal. Upon subjecting this surface
25 to the action of intense ultrasonic vibrations in an
inert medium such as water, the nonadherent portions
of the film quickly break off from the adherent regions
and fall off from the ceramic surface leaving only the
self-aligned, adherent alloy coating on the refractory
30 metal featues. This is how the objective of selectively
coating of the refractory metal features on the sub-
strate surface with an adherent coating of a copper-
palladium alloy conductive to joining to associated
elements through the use of common, low temperature

brazing and soldering alloys, was achieved without
using any selective masking steps.

The essential condition for the success of this process
5   is the promotion of selective adhesion of the deposited
films to the refractory metal features on the substrate
surface while concurrently causing this film to debond
from the bare ceramic surface. To bring this about the
following conditions were needed: (i) The choice of two
10   suitable metals of widely differing melting points
which form a continuous series of solid solutions whose
solidus curve lies intermediate between the melting
points of the two component metals, (ii) The first
metal to be deposited on the substrate surface should
15   be the metal whose melting point is lower of the two,
and which in the molten state wets well the refractory
metal to be coated, (iii) The thicknesses of the de-
posited layers and the heating rate chosen being such
as to ensure the formation of a temporary liquid layer
20   next to the substrate surface at or below the peak heat
treatment temperature while the top portions of the
composite film remains unmolten, (iv) The relative
thicknesses of the metal layers are chosen to ensure
that the solidus temperature of the completely homo-
25   genized alloy stays safely above the peak heat treating
temperature and (v) The total thickness of the coating,
while chosen to be adequate for subsequent joining of
associated elements to the refractory metal features,
should not be excessive so as not to need excessive
30   times of ultrasonic vibration exposure for the removal
of the parts of the film rendered nonadherent to the
bare ceramic surface by the heat treatment.

Referring to Fig. 1, there is depicted a fired ceramic
35   substrate 1, typically a multilayered ceramic substrate

FI 981 031 / FI 981 032

which can be produced by the method described in detail
in US Patent 3 518 756. Although Figs. 1 to 5 are illus-
trated in broken section, the internal metallurgical
conductor pattern is not shown since it does not con-
5   stitute a material part of the invention. It is also to
be understood, however, that substrate 1 need not be a
multilayer ceramic substrate, but could be solid with
the metallurgical layers formed entirely on the sur-
faces. The material of substrate 1 is normally formed
10 of alumina, or alumina plus other materials (such as
glass), or a ceramic glass material. The surface of
substrate 1 shows metallurgy areas 2 and 3 (of via hole
4) which are normally formed of a refractory metal
(such as a molybdenum based metal) which was deposited
15 prior to sintering of substrate 1.

For one development of the first embodiment of the
invention, the substrate 1, inclusive of metallurgy
circuit features 2 and 3, are blanket coated to a
20 thickness of about 2 to about 5 µm, as by sputtering
and vacuum evaporation, with a low melting point metal
(e.g. copper M.P. 1083°C). The low melting point layer
5, is in turn suitably coated with a blanket layer 6 of
a higher melting point metal to a thickness of about 2
25 to about 5µm. The metal of layer 6 can be any suitable
higher melting metal such as palladium, platinum, and
nickel which form a continuous series of solid solu-
tions with copper with the solidus points of all such
solid solutions lying intermediate between the melting
30 point of copper (1083°C) and the melting point of the
metal chosen for layer 6. Also, the top metal layer 6
can also comprise a refractory metal such as molybdenum,
tungsten and the like. It is only necessary that the
low melting point bottom metal layer 5 which will, in
35 its liquid form wet the circuit features 2 and 3, and

dewet the bare or unpatterned surface areas 7 of sub-
strate 1.

The composite metal 5/6 coated substrate is then heated
5   to a temperature between the melting points of the
bottom and top (5 and 6) layer metallization, whereby
the top layer 6 remains as a nonliquid solid film sand-
wiching against substrate 1, a captive liquid zone 5A
formed of the molten layer 5. For a system utilizing a
10 bottom copper layer 5 and a top palladium or nickel
layer 6, the substrate can be heated to about 1100-
1140°C.

With the use of a refractory metal, such as molybdenum
15 for top layer 6 in conjunction with a bottom copper
layer 5, the suructure can be heated to about 1100°C.
Although the temperature of the heat treatment will
vary with the system of the top and bottom layers 5/6,
it can extend in the range from the melting point of
20 the metal of layer 5 to the solidus temperature of the
alloy formed by the complete mixing of layers 5 and 6.

During heat treatment the molten bottom metal layer 5A
brazes or bonds to the molybdenum circuit features 2
25 and 3, while dewetting the unpatterned surface areas
7 of substrate 1, on contact therewith where it de-
bonds at 20, on cooling from the substrate surface.
The solidified liquid alloy is identified as 5B.

30 After cooling, the metallization of bottom and top
layers 5 and 6, can be suitably removed as by sand
blasting and wire brushing, or by subjecting the
substrate to an ultrasonic cleaning operation or
other suitable medium, in a conventional tank type

of ultrasonic cleaner having side and/or bottom
mounted transducers.

In the absence of the more refractory palladium layer
5   or the copper layer, the latter would be completely
molten at the peak heat treating temperature and would
freely flow on the uneven surface of the substrate
forming puddles bridging over closely spaced refrac-
tory metal features at the low spots on this surface,
10   these bridges remaining as solid copper bridges across
these features upon cooling. The molten copper will
also form a multitude of small spherical droplets on
the ceramic surface which will remain as copper spheres
tenaciously attached to the asperities on the ceramic
15   surface. Thus the presence of the more refractory pal-
ladium (or nickel) over the liquid metal layer during
the heat treatment (Fig. 3) acts to prevent the lat-
ter's tendency for lateral flow on the substrate sur-
face, as well as to prevent the balling up of the
20   molten copper on the ceramic because it will remain
spread on the solid metal crust. If during the heat
treatment no liquid zone is formed, which can happen
if the peak heat treatment temperature attained is be-
low the melting temperature of the alloy composition
25   closest to the ceramic surface at the instant of reach-
ing that temperature, no selective bonding of the film
to the molybdenum surface will occur. Such a condition
could arise if (i) the heating rate is so slow as to
allow considerable penetration of palladium into the
30   region of the copper layer adjacent to substrate sur-
face prior to attaining the peak heat treating temper-
ature (ii) the thickness of the copper layer is not
adequate for the heating rate employed, to prevent
excessive palladium penetration into the copper layer
35   prior to reaching the peak temperature for the heating

rate employed. Thus the critical heating and the copper
layer thickness are interdependent. These also depend
on the rate of change of the solidus temperature with
composition (i.e., the slope of the solidus curve) on

5   the copper-rich side of the binary phase diagram for
the two metals and on their interdiffusion rates. Thus,
the gentler slope of the solidus curve in the copper-
palladium system would allow for a greater degree of
palladium penetration into copper layer prior to

10 reaching the peak heat treating temperature, than in
the case of the copper-nickel system which exhibits
a steeper solidus curve.

The relative thicknesses of the copper and palladium

15 (nickel) layers should be so chosen as to ensuure that
the solidus temperature of the completely homogenized
alloy that will result from their eventual, complete
mixing be safely above the peak temperature chosen for
the heat treatment to prevent its complete melting at

20 this temperature. In the case where the top layer chosen
is such that it does not form any intermetallics or
solid solution with the layer below (e.g., molybdenum
over copper), the top layer thickness need only be
sufficient to prevent the breakout of the molten copper

25 through it during the heat treatment. The mechanism of
film removal involves the rupturing of the loose metal
film 5 from the substrate areas by the action of the
shock waves impinging on the surfaces. The shock waves
being induced by bubble collapse (cavitation) within

30 the liquid medium during the ultrasonic action. One pre-
ferred form of removing the metal film 5 is by use of
an ultrasonic horn to focus and deliver very high local
intensities of energy (about 100 watts per cm^2) and by
utilizing the near field characteristics of the ultra-

35 sonic field close (e.g. about 1 to about 10 mm) to the

horn surface where cavitation plays only a minor role.
In such an arrangement, the removal of the loosely ad-
herent metal films 5 from the substrate surface is very
efficient. For example, non-adhering copper-palladium

5 films of 5 μm thickness can be removed from alumina
ceramic surfaces in about 5 to about 30 seconds.

It is believed that the mechanism of metal film removal
is as follows: In the near-field region, there exists a

10 coupling of the ultrasonic field (generated by the
transducer) to the surface of the substrate carrying
the metal film. Where the metal film 5 is strongly ad-
hering to the substrate, such as in areas of the pre-
existing metallurgical circuit features under the film,

15 the ultrasonic energy is merely transmitted through the
metal film 5 into the substrate and dissipated. Where
the metal film 5 is non-adhering, such as on the bare
substrate surface areas, the ultrasonic energy is sub-
stantially absorbed by the thin metal film 5, causing

20 it to vibrate with the field. This vibration generates
alternating stresses at points of the film where it
adheres to the substrate which eventually causes the
film breakage at these points. High frequencies (e.g.
10-40 KHz) of the field ensures that from 10-40 X 10^3

25 cycles of alternating stress is applied to the metal
film 5 at the boundaries of adhering regions so that
the fatigue limit for the film is reached in 1 to 30
seconds depending on the nature of the metal film, its
thicknesses, and the distance between adjacent adhering

30 areas. With the complete removal of the non-adhering
metal film 5 from the substrate surfaces, only the
pre- existing metallurgical circuit features 2A on the
substrate will retain an adherent metal film 6/2A, as
shown in Fig. 5.

FI 981 031 / FI 981 032

Where a refractory metal is employed as the top layer
6, it can be removed from the final structure, where
desired or required, by suitable wet or dry etching
techniques.

5

Where limitations of heating furnaces and heat-up and
cool-down present problems of temperature exposures,
one effective method of heating is by E-beam. Use of
an E-beam will heat the substrate to temperature very

10   quickly with subsequent rapid cooling. Illustratively,
the structure can be heated with a plused electron
beam or laser beam to locally heat up the metal layers
and cause melting of the bottom metal layer 5 in small
areas in a very short time. Since the heat duration is

15   quite small, the MLC substrate should not feel appre-
ciable thermal shock. After the E-beam or laser heat
treatment, the unwanted regions (e.g. over the unpat-
terned surface areas 7 of substrate 1) can be removed
by various techniques.

20

Illustratively for Cu-Pd alloy capping of the circuit
features 2 and 3, a 2 μm film of copper was used for
bottom layer 5 with a blanket coating of 1 μm of pal-
ladium for the top layer 6, the unit was heat treated

25   to 1100°C in a forming gas ambient as follows:

        2 1/2 hours heating time to 1100°C.
        5 minutes hold at 1100°C
        Furnace, off to cool

30

The substrate was subsequently cleaned ultrasonically
to completely remove the non-adhering alloy film on the
unpatterned surface areas 7 of an alumina ceramic sub-
strate 1. An adherent Cu-Pd alloy cladding remained on

35   the molybdenum circuit features 2 and 3.

FI 981 031 / FI 981 032

Second Embodiment

The method according to the second embodiment enables
the selective coating of surface metal features of di-
5 electric substrate with a cladding of diverse metals
or their alloys to obtain desired characteristics such
as solderability, brazeability and/or corrosion resis-
tance. The coatings are formed first by blanket deposi-
tion over the substrate, inclusive of existing metal-
10 lurgical pattern features, with pattern definition
occuring solely due to a subsequent heat treatment in
a suitable ambient.

For bimetallic coatings, two suitable alloyable metals
15 are chosen which form a continuous series of solid
solutions showing a negative deviation from Raoult's
law. Illustrative of these systems are the combinations
Pd/Ni, Au/Ni and Au/Cu as shown in their respective
phase diagrams of Figs. 6-8. These metal systems when
20 molten, dewet the substrate surface with good wetting
and adhesion to the metallurgical pattern surfaces. The
coated substrate is heated to a temperature (T_H) above
the lowest liquidus line of the metal coatings but be-
low the melting points of either pure metal component.
25 Due to heating, the metal coatings interdiffuse to form
a range of compositions which are changing with time.
The thin layer in the dual coating whose composition
can melt below T_H becomes liquid, and with time this
molten zone can move up or down; and when it reaches
30 the surfaces of the substrate and the metallurgical
pattern, localized selective adhesion is obtained, e.g.
on the pattern but not on the bare substrate surfaces.
At this point the surface tension of the liquid zone
causes a metal film to strongly braze or bond to the
35 metallurgical pattern and to debond from the bare sub-

FI 981 031 / FI 981 032

strate surfaces, from which, after cooling, it can be
mechanically removed as by wire brushing, light sand
blasting and, preferably, ultrasonically.

5   For example, in application to the semiconductor art
utilizing an alumina MLC substrate having molybdenum
based circuit features, the specifically noted alloy
systems are particularly advantageous. Illustrative of
these systems is palladium and nickel which forms an

10 excellent brazing alloy for molybdenum, since it is
solderable and brazeable while providing effective
corrosion resistance for molybdenum. The heat treatment
can be effected at a T_H of about 1250 to about 1300°C,
which can be accommodated in the temperature hierarchy

15 of the processes and materials of the MLC. The temper-
ature of heat treatment is chosen by reference to the
phase diagram, as for example Fig. 6 for Pd/Ni system.
This temperature should be at or slightly above the
lowest liquidus temperature in the system, which for

20 the Pd/Ni system is 1250°C at a 60% Pd/40% Ni composi-
tion. The choice of solid solution systems exhibiting
a negative deviation from Raoult's law need only enable
a heat treatment temperature that should lie above the
liquidus line in the system but not exceed the melting

25 points of either pure metal component.

During heat treatment of the illustrative Pd/Ni system,
the component metals interdiffuse forming a series of
solid solutions across the coating thickness. When a

30 particular segment of this interdiffused region attains
the composition 60% Pd/40% Ni, this segment will become
liquid. As the interdiffusion continues, the thin
liquid zone 18 (Fig. 10) initially formed at the Pd-Ni
interface will further enrich itself with palladium or

35 nickel causing it to freeze. However, another segment

FI 981 031 / FI 981 032

in the diffusion zone will now be at the critical com-
position and will melt. This dynamic process continues
repeatedly, with the effect of moving a thin liquid
zone 18 gradually towards the substrate surface, to,
5   in effect, form a floating zone moving to the sub-
strate, see 18A, Fig. 11.

When this floating zone (Fig. 11) reaches the surface
of the existing metallurgy (e.g. molybdenum) of the
10 substrate, it will wet the metal and cause the alloy
deposit to braze to it. However, when simultaneously
the liquid zone reaches the bare or unpatterned sub-
strate surfaces, it will dewet from the surface (e.g.
alumina ceramic), and the strong tension forces will
15 cause the deposit to debond from the surfaces (Fig.
12). The debonded metal layer portion 14A from the
ceramic surface 12 can be easily removed, as by brush-
ing and, preferably, ultrasonic cleaning in which only
the metallurgical pattern 3 will be selectively coated
20 with an adherent Pd/Ni alloy layer 14 (Fig. 13).

Referring to Figs. 9 to 13, there is shown a fired
ceramic substrate 1, typically an alumina based mul-
tilayered ceramic substrate which can be produced by
25 the method described in detail in US Patent 3 518 756.
Although Figs. 9 to 13 are illustrated in broken sec-
tion, the internal metallurgical conductor pattern is
not shown in detail since it does not constitute a ma-
terial part of the invention. Also, it is to be under-
30 stood, however, that substrate 1 need not be a multi-
layer ceramic substrate, but could be solid with the
metallurgical pattern formed entirely on the surfaces.
However, for this embodiment a portion of the metal-
lurgical pattern, of an MLC, is shown in the context
35 of via extensions or studs 3, which can be formed of

a refractory based metal, such as molybdenum which
was deposited in a via of the substrate 1 before its
firing. The material of the substrate 1 is typically
formed of alumina or alumina plus other materials
5   (such as glass), or a ceramic glass material.

The substrate 1, inclusive of the metallurgical feat-
ures 3, are blanket coated in an E- beam evaporation
system sequentially with 1-5 μm thick coatings of a
10   nickel film 16 and a palladium film 17, in that order.
However, as noted above, the dual coatings can comprise
other systems, such as Au/Ni, Au/Cu, which conform to
this invention. The thickness of the films need not be
the same, and each may vary in thicknesses of about 1
15   to about 5 μm.

The composite metal 16/17 coated substrate is subse-
quently heat treated in an H_2 ambient at temperatures
of 1300-1350°C, holding at this peak temperature for
20   2 hours. Although most thin metallic films (in the
micron range), evaporated or sputtered, exhibit poor
discrimination in adhesion between the substrate sur-
faces (e.g. ceramic) and the metallurgical pattern
(e.g. molybdenum) liquid metals and their alloys (e.g.
25   Cu, Cu/Pd, Au etc.), on the other hand wet the metal-
lurgical pattern (Mo) and dewet the substrate (e.g.
ceramic) substrate. The layer thicknesses of Pd and Ni
and the peak heat treatment temperatures will be so
chosen that the latter lies safely below the solidus
30   point for the completely homogenized Pd-Ni alloy that
results.

On cooling of the substrate a layer of palladium-nickel
alloy will remain over the surface of the substrate,
35   this layer having become strongly adherent to the re-

FI 981 031 / FI 981 032

fractory metal features in the substrate while delami-
nating from the bare ceramic areas of the substrate
surface. The delaminated portions of the alloy film
can be easily detached from the surface by light sand
5 blasting, wire brushing or ultrasonic cleaning. The
results are displayed in Figs. 14 and 15 which, respec-
tively, show the via regions and EC pads, of a sample,
showing Pd/Ni coated molybdenum circuit features and
the absence of any bridge in between the conductors.
10 Fig. 16 shows a cross-section through a via 30 con-.
firming the formation of a continuous adherent layer 14
of Pd/Ni alloy.

The ultrasonic cleaning can be effected by conventional
15 methods utilizing suitable mediums in a conventional
tank type of cleaners having side and or bottom mounted
transducers. The mechanism of film removal in ultrasonic
cleaning involves the rupturing of the loose metal film
areas 14A from the substrate areas by the action of the
20 shock waves impinging on the surfaces. The shock waves
being induced by bubble collapse (cavitation) within
the liquid medium during the ultrasonic action. One pre-
ferred form of removing the metal film areas 14A is by
use of an ultrasonic horn to focus and deliver very high
25 local intensities of energy (about 100 watts per cm^2)
and by utilizing the near field characteristics of the
ultrasonic field close (e.g. about 1 to about 10 mm) to
the horn surface where cavitation plays only a minor
role. Under such conditions, the removal of the loosely
30 adherent metal film areas 14A from the substrate sur-
face is very efficient. For example, non-adhering pal-
ladium-nickel films of 5 μm thickness can be removed
from alumina ceramic surfaces in about 5 to about 30
seconds.

FI 981 031 / FI 981 032

It is believed that the mechanism of metal film removal
is as follows: In the near-field region, there exists a
coupling of the ultrasonic field (generated by the
transducer) to the surface of the substrate carrying

5   the metal film. Where the metal film 14 is strongly ad-
hering to the substrate, such as in areas of the pre-
existing metallurgical circuit features under the film,
the ultrasonic energy is merely transmitted through the
metal film 14 into the substrate and dissipated. Where

10   the metal film 14 is non-adhering, such as on the bare
substrate surface areas, the ultrasonic energy is sub-
stantially absorbed by the thin metal film 14, causing
it to vibrate with the field. This vibration generates
alternating stresses at points of the film where it

15   adheres to the substrate which eventually causes the
film breakage at these points. High frequencies (e.g.
10-40 KHz) of the field ensures that from $10\text{-}40 \times 10^3$
cycles of alternating stress is applied to the metal
film 14 at the boundaries of adhering regions so that

20   the fatigue limit for the film is reached (in 1 to 30
seconds) depending on the nature of the metal film, its
thicknesses, and the distance between adjacent adhering
areas. With the complete removal of the non-adhering
metal film areas 14A from the substrate surfaces, only

25   the pre-existing metallurgical circuit features 3 on or
recessed in the substrate will retain an adherent metal
film 14, as shown in Fig. 16.

FI 981 031 / FI 981 032

0089604

C L A I M S

1. Method for selectively depositing metal coatings
   over an existing metallurgical pattern supported
   on or recessed in a dielectric substrate, charac-
   terized by the following steps:

5

   A) sequentially blanket coating said substrate
      and said pattern with metals tuned to another
      in such a way that on heating a liquid metal
      or alloy layer is formed adjacent the sub-

10   strate and pattern surface where said layer
      wets said pattern but not said substrate;

   B) heating the then present structure to a tem-
      perature where said liquid metal or alloy

15   layer is formed;

   C) cooling said structure; and

   D) removing said metals from the surface of said

20   substrate not covered by said pattern.

2. Method according to claim 1, wherein said metal
   coatings consist of brazeable and solderable
   metals.

25

3. Method according to claim 1 or 2, wherein said
   dielectric substrate is comprised of a ceramic,
   like an alumina based ceramic.

30 4. Method according to any one of claims 1 to 3,
   wherein said metallurgical pattern is comprised
   of a refractory based metal.

0089604

5. Method according to claim 4, wherein the refrac-
    tory metal is selected from the group of molyb-
    denum and tungsten.

6. Method according to any one of claims 1 to 5,
    wherein said coatings are ultrasonically removed
    from said bare substrate surface areas.

7. Method according to any one of claims 1 to 6,
    wherein the following process steps are executed

    A) sequentially blanket coating said substrate
        (1), inclusive of said pattern (2, 3), with
        discrete levels of diverse metals having a
        differential in melting points (a) bondable
        to said pattern (b) non-wetting to the bare
        surface (7) of said substrate (1), with the
        metal having the lowest melting point dis-
        posed adjacent said substrate;

    B) heating the then present structure to a tem-
        perature above the melting point of the lower
        melting metal;

    C) cooling said structure to delaminate the
        metal coatings on the bare surfaces (7) of
        said substrate (1); and

    D) removing said delaminated coatings from the
        bare surface areas of said substrate (1) to
        retain a bonded cladding comprised of said
        metals on said metallurgical pattern (2, 3).

FI 981 031 / FI 981 032

8. Method according to claim 7, wherein said diverse metals form alloy systems and show a behaviour according to Raoult's law or a positive deviation from it and wherein the temperature in said heat-
5 ing steps does not exceed the liquidus temperature of any resultant completely homogenized alloy corresponding to their amounts of metals deposited.

9. Method according to claim 7 or 8, wherein the sub-
10 strate (1) adjacent metal is selected from the group of copper, nickel, nickel/palladium alloy and copper/palladium alloy.

10. Method according to claim 7, wherein the following
15 process steps are executed

A) depositing a blanket coating of a first metal layer (5) over said substrate (1), inclusive of said pattern (2, 3) with said first metal
20 layer (5) having a melting point lower than that pattern and being adherent thereto;

B) depositing a blanket coating of a second metal layer (6) over said first metal layer
25 (5), with said second metal layer (6) having a melting point higher than that of said first metal layer (5);

C) heating the then present structure to below
30 the melting point of said second metal layer (6) and above said of said first metal layer (5) for selective melting thereof; and

FI 981 031 / FI 981 032

D)   removing said first and second metal layers
      (5, 6) from the unpatterned surface areas (7)
      of said substrate (1).

11.   Method according to claim 10, wherein said first
      metal layer (5) is selected from the group of
      copper, nickel and gold based metals.

12.   Method according to claim 10 or 11, wherein said
      second metal layer (6) is comprised of a refrac-
      tory metal.

13.   Method according to claim 12, wherein the step of
      selective removal thereof from the cladding on
      said pattern (2, 3) is included.

14.   Method according to any one of claims 1 to 6,
      wherein the following process steps are executed

A)   sequentially blanket coating said substrate
      (1) inclusive of said pattern with discrete
      levels of diverse alloyable metals (16, 17)
      showing a negative deviation from Raoult's
      law in their phase diagram with the alloy
      of said metals bondable to said pattern and
      non-wetting to the bare surfaces (12) of said
      substrate;

B)   heating the then present structure to a
      temperature below the melting point of
      said metals (16, 17) and above the lowest
      liquidus temperature in the phase diagram
      of the alloy system of said metals (16, 17),
      whereby a cladding of said metals (16, 17)
      is bonded to said pattern and form loosely

adhered segments (14A) on said bare surfaces
(12) of said substrate (1);

C)   cooling said structure; and

5

D)   removing said segments (14A) from said bare
surfaces (12) of said substrate (1).

15.   Method according to claim 14, wherein said metals
10   are selected to form one of Pd/Ni, Au/Ni and Au/Cu
binary alloy systems.

16.   Method according to claims 14 or 15, wherein said
metallurgical pattern comprises contact points on
15   the surfaces of said substrate (1) for solder or
brazing elements thereto.

17.   Method according to any one of claims 14 to 16,
wherein said substrate (1) is a multilayer ceramic.

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

0089604

FIG. 9

17
16
3
3
1
3
1

FIG. 10

17
16
3
18
3
1

FIG. 11

3
18A
3
1

FIG. 12

14
12 14A
3
1

FIG. 13

14
14
1
3
3
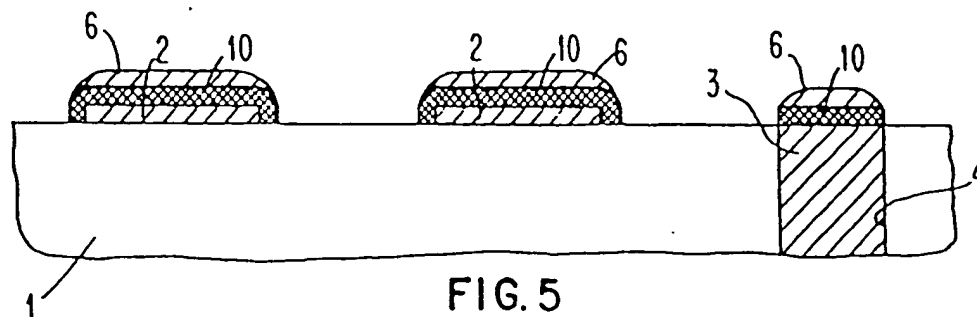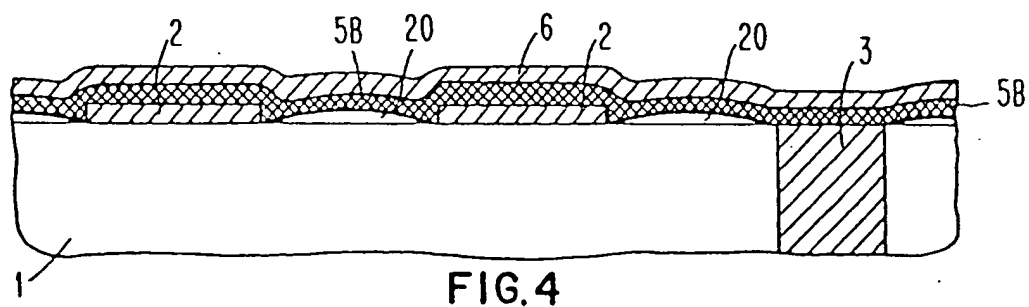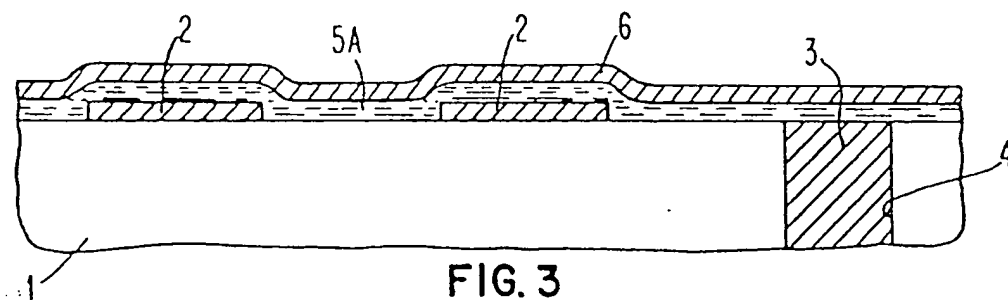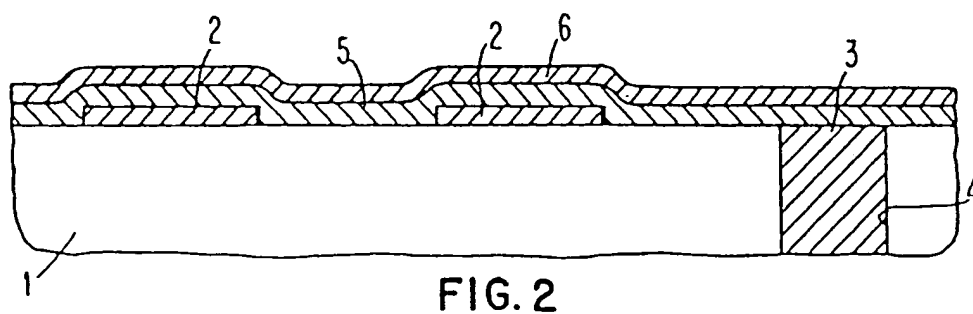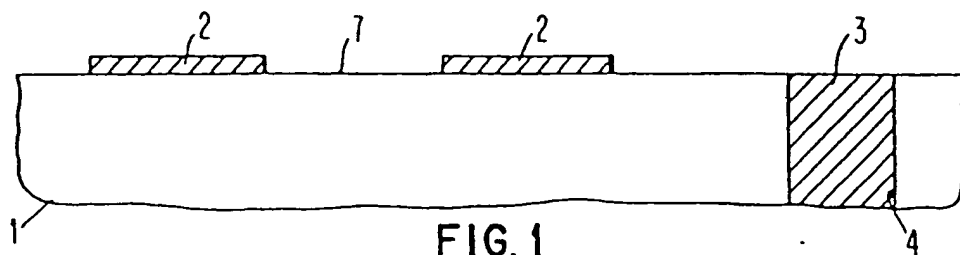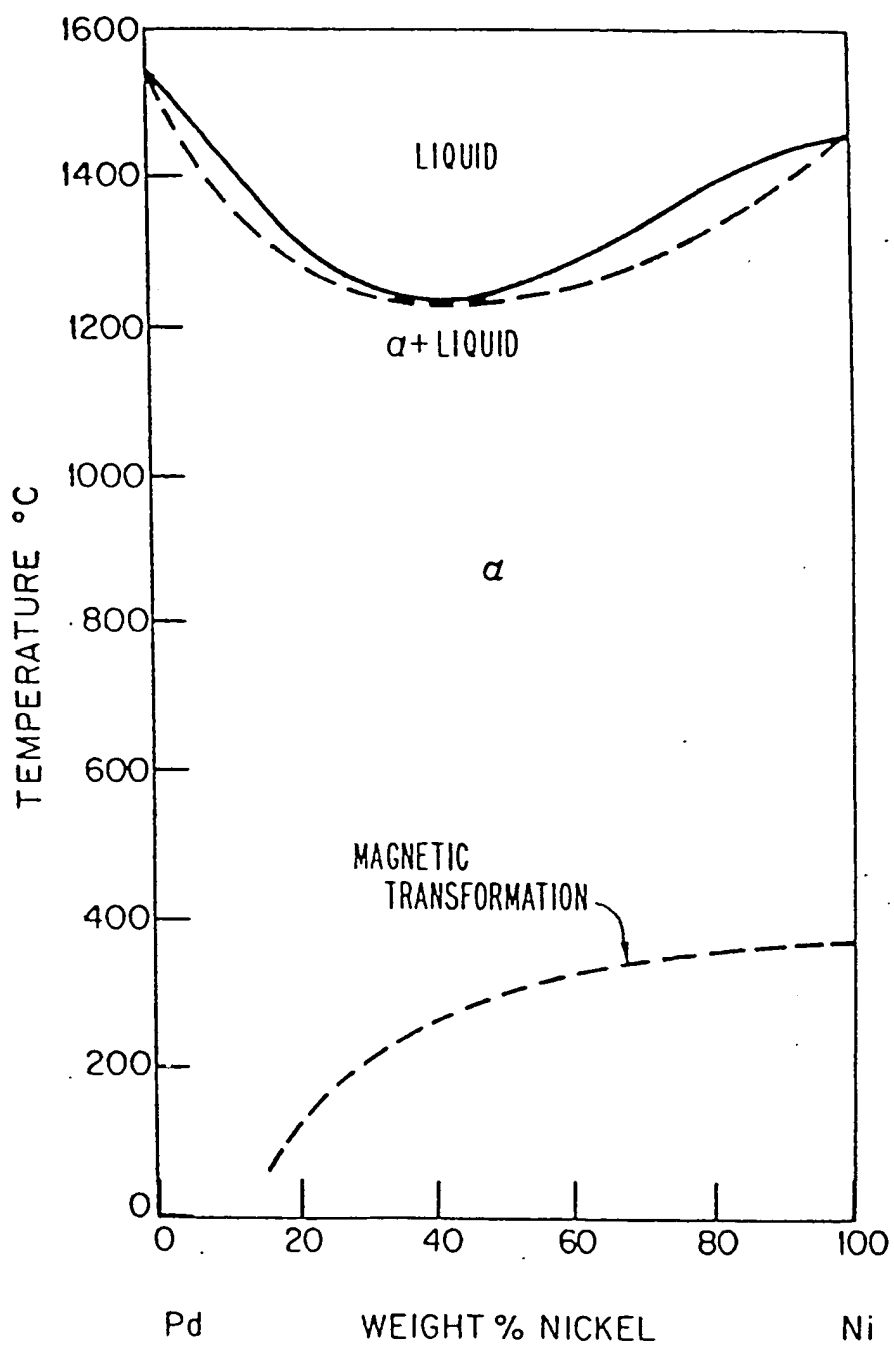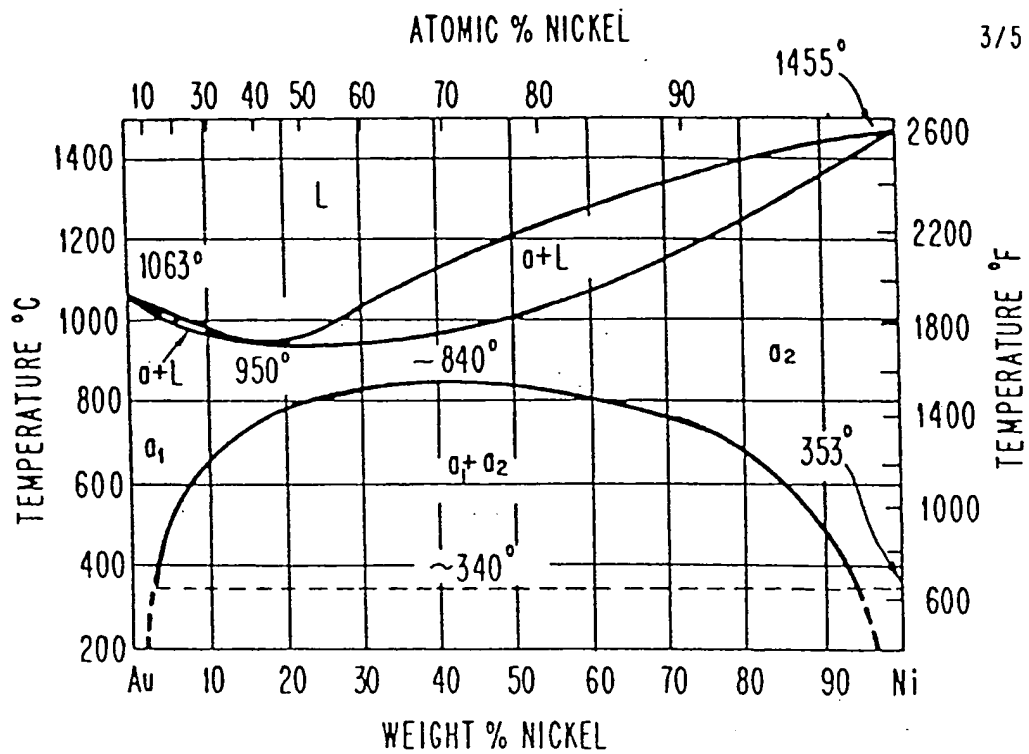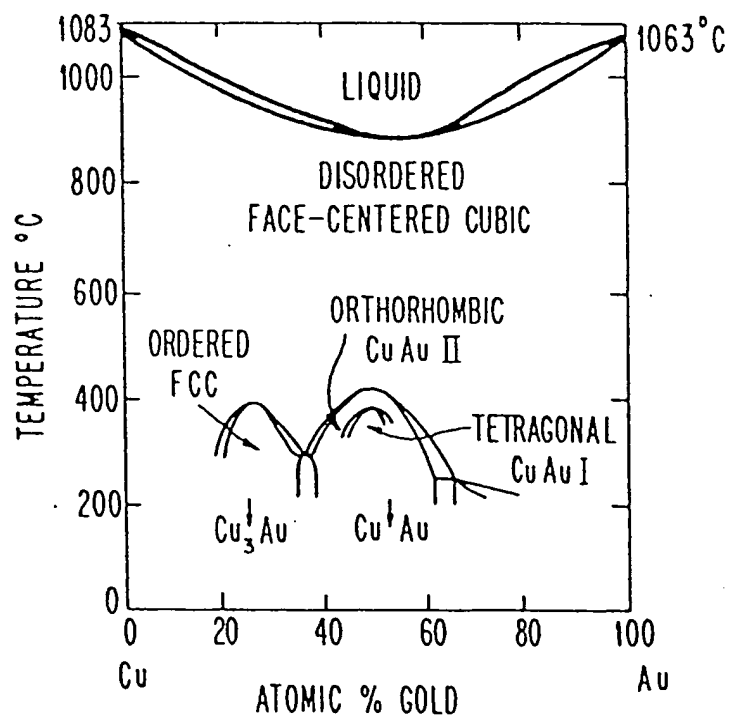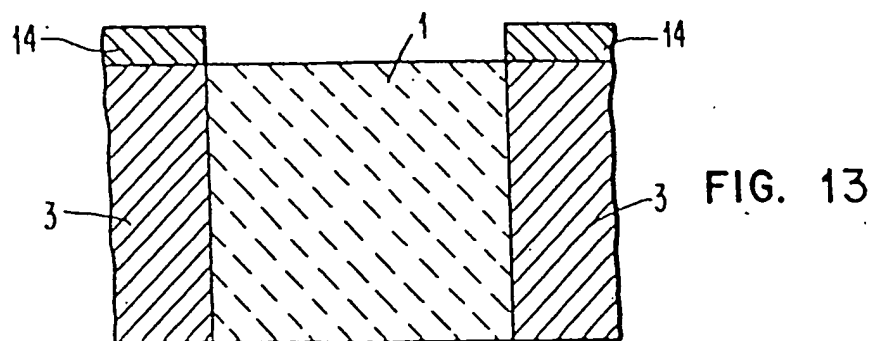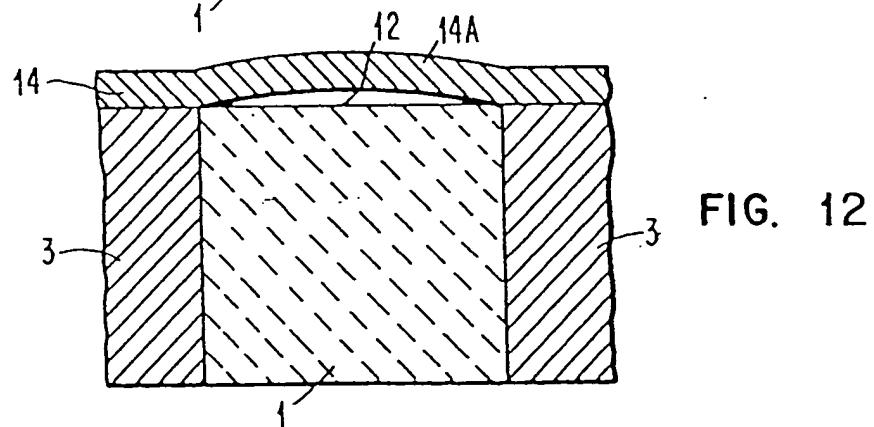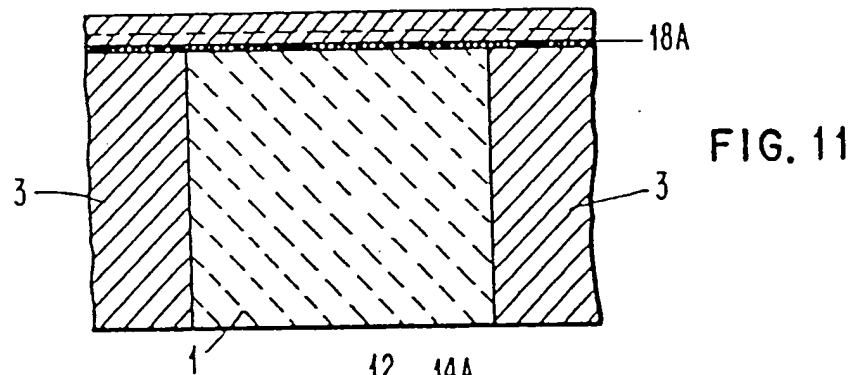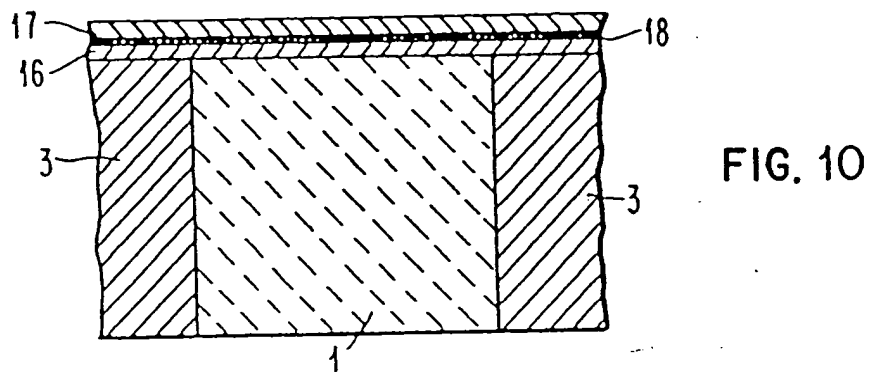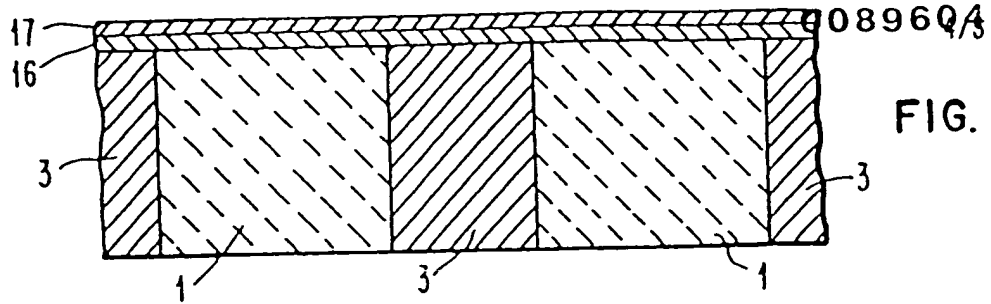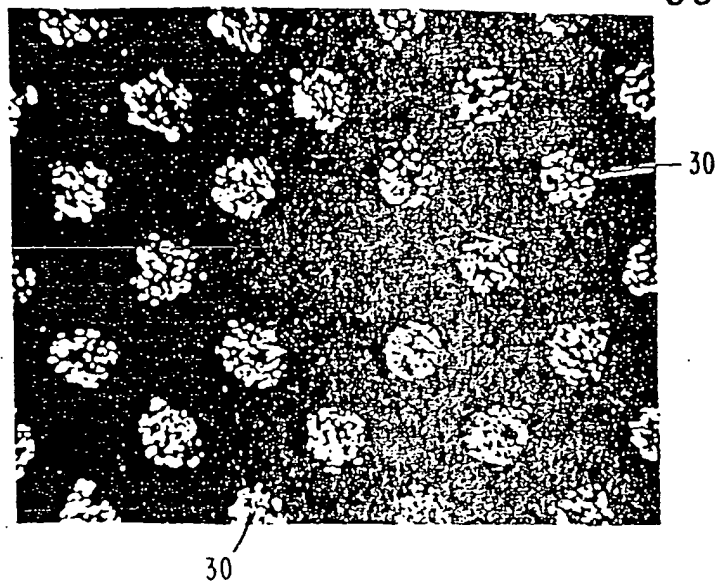
FIG. 14

FIG. 15

FIG. 16

0089604

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 83102539.0

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
A	DE - A1 - 2 745 581 (INTERNATIONAL BUSINESS MACHINES CORPORATION) * Claims * --	1	C 23 C 5/00 C 23 C 17/00 C 04 B 41/14// H 01 L 21/88 H 01 L 21/288 H 05 K 3/00
A	DE - B2 - 2 453 035 (INTERNATIONAL BUSINESS MACHINES CORPORATION) * Claims; fig. * --	1	
A	DE - B2 - 2 443 287 (SIEMENS AG) * Claims * --	1,4,9, 11,15	
A	US - A - 3 945 113 (M. BONNEL) * Claims; fig. * ----	1,9,11, 15	

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 23 C
C 04 B
H 01 L
H 05 K

The present search report has been drawn up for all claims

Place of search VIENNA	Date of completion of the search 08-06-1983	Examiner SLAMA

EPO form 1503 03 82